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RADIOCARBON FROM PILE GRAPHITE;

CHEMICAL METHODS FOR ITS CONCENTRATION

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RADIOCARBON FROM PILE GRAPHITE;

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ABSTRACT

Samples of pile graphite, irradiated in a test-hole at Hanford for 15 months, have been assayed for radioactive C^{14}, yielding 0.38 ± 0.04 microcuries per gram. At this level of activity, the pile graphite contains very valuable amounts of C^{14}. The relation between the above assay and the probable average assay of pile graphite is discussed, and it is concluded that the latter is almost certainly above 0.3 uc/gram.

Controlled oxidation of this graphite, either with oxygen at $\sim 750^{\circ}C$, or with chromic acid "cleaning solution" at room temperature, yields early fractions which are highly enriched in C^{14}. Concentrations of 5-fold with oxygen, and 50-fold with CrO_3, have been observed. The relation between the observed enrichment and the Wigner effect is discussed, and a mechanism accounting for the observations put forward. According to this, about 25% of the stable carbon atoms in the lattice have been displaced by Wigner effect, a large fraction of which have healed by migrating to crystal edges. All the C^{14} atoms have been displaced, and the same fraction of these migrate to the edges. The enrichment then results from surface oxidation, in the oxygen case. Predictions are made on the basis of this hypothesis.

A technique of counting radioactive CO_2 in the gas phase is described.

I. Introduction

The tremendous neutron fluxes occurring in a pile make otherwise negligible neutron-induced phenomena observable.[1] Thus the 0.3 barn capture cross-section of C^{13} to form C^{14} which is unobservable in any other way becomes important. It is the principal purpose of this report to present and discuss certain data on C^{14} production by this method obtained on samples of the Hanford graphite.

Samples of Hanford graphite taken from bar R, completely burned to CO_2 yield activities of 0.38 ± 0.04 microcuries per gram (the method of counting will be described in the final section). These samples had been exposed in a "test hole" for 15 months. We shall assume the above value to be a typical assay subject to limitations discussed below. At this level the 6000 tons of graphite in the piles contain some 2000 curies of radiocarbon - a quantity large enough to supply tracer carbon for many uses for the whole nation for years. While the material as found, or enriched by a small factor, is of rather low specific activity compared to nitrogen-produced C^{14}, its activity is more than sufficient for most chemical problems and a wide variety of biological ones.

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[1] A. Langsdorf, Report No. DP-3272

It should be set aside for this purpose at any time that the piles cease operation, and plans made for its useful dispersal.

II. Validity of the Assay

A number of variables affect the reliability of the estimate given above for the C^{14} content of the Hanford graphite. A few of the more important will be discussed below.

To begin with, it may be of interest to calculate, from Langsdorf's value of the C^{13} cross-section, the expected concentration of C^{14} in the pile graphite. We have that

$$\frac{10^{-24} \cdot 0.3 \cdot 0.01 \cdot 6 \cdot 10^{23} \cdot 10^{13} \cdot 5 \cdot 10^{7}}{12} = 7 \cdot 10^{16} \text{ atoms } C^{14}/\text{gm}$$

$$\approx 1.5 \ \mu c/\text{gm}$$

using Langsdorf's provisional half-life (25,000 years), which was used in his cross-section calculation. Thus the expected value of the assay (though admittedly very rough) is about four times the observed value (assuming a mean flux of 10^{13} for thermal neutrons).

The first important difference between bar R and the average sample of Hanford graphite is a difference in neutron flux. While the value for the neutron flux in the test hole relative to that in the body of the pile is not known, it is almost certain to be less. This would tend to make the ob-

served assay lower than the true one.

The second factor is the possibility that air in the interstices of the test-hole bar contained sufficient N_2 to account for the formation of most of the C^{14} by the $N^{14}(n,p)C^{14}$ reaction. The pile graphite, having been in a helium atmosphere for a long period, would not contain C^{14} formed in this manner.

The first point is the fraction of the graphite volume which is occupied by the intergranular interstices. This appears to be about 25%, varying between 20% and 30%.[2]

The flux of 10^{13} thermal neutrons/cm^2/sec and the 1.7 barn cross-section for the $N^{14}(n,p)C^{14}$ then enable us to calculate the yield of C^{14} if air were present at a definite pressure of 1 atm. This gives

C^{14} yield (curies/gm/day) =

$$\frac{1}{\rho} \cdot \frac{.69}{t_{\frac{1}{2}} \cdot 3.17 \cdot 10^7} \cdot \frac{1}{3.7 \cdot 10^{10}} \cdot 1 \cdot 10^{19} \cdot 1.7 \cdot 10^{-24} \cdot 10^{13} \cdot 8.6 \cdot 10^4 \cdot 0.25$$

$$= \frac{2.15 \cdot 10^{-6}}{\rho \, t_{\frac{1}{2}}(\text{yrs})}$$

where ρ is the apparent density of the graphite (1.7 gms/cc) and $t_{\frac{1}{2}}$ is the C^{14} half-life in yrs. Table I gives the values for $1\frac{1}{2}$ yr exposures for the three reported values for the half-

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[2]Information from Drs. Simpson and Neubert

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life of C^{14}.

TABLE I

Yield ($\mu c/gm/1.5$ yrs)	$t_{\frac{1}{2}}$ Value (yrs)	Remarks
0.0280	25,000	Langsdorf value
0.108	6,600	Snell value
0.2804	2,400	Dunning value

The third point is the time for elutriation of the intergranular air from a cylinder of graphite continuously purged externally by a He stream. Measurements of the diffusion of He have been made on typical AGOT graphite by Dr. Burton's Metallurgical Laboratory Group.[3] A recalculation of their data gives a value of about 10 cm^2/min for the self diffusion coefficient of He through the graphite at one atmosphere total pressure and $30^{\circ}C$. A theoretical estimate of the value for air can be made by noting that the void fraction, Θ , also is the fraction open area in any given plane through the sample, providing the intergranular spaces are randomly oriented. This means that the diffusion coefficient for air in a perfectly stagnant air-He mixture is likely to give a good value for the corresponding coefficient for a porous graphite when multiplied by Θ . Since the diffusion coefficient for

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[3]Memo Burton to Hilberry, MUC-MB-283, Sept. 15, 1944

N_2 in air at room temperature is 30 cm^2/min we expect a value between 6 and 9 cm^2/min for the graphite. This argument together with the value from the Burton data gives us some confidence in a D value of about 10 cm^2/sec for our problem.

Having the D value we estimate the time for removal of about half of the air by the Einstein relation

$$\ell^2 = 2 \, Dt$$

where ℓ is the distance diffused and t is the time. From this we see that a rod even 10 cm in radius would have a purge half-time of about 6 minutes and we conclude that relatively complete removal of the air occurs in a few hours at most.

On the basis of the probability that the purge is relatively rapid it seems likely that the test hole purge was relatively effective. This taken together with the values for the maximum possible production by intergranular air which are themselves less than the observed assay of 0.38 μc/gm leads us to the conclusion that probably the major portion of the activity in the test hole sample arises from the $C^{13}(n, \gamma)C^{14}$ reaction and that we are relatively certain on this basis that assay of the main body of the piles residing in the helium atmosphere will reveal at least 0.3 μc/gm on the average. Finally, the extra time of irradia-

tion between the removal of bar R and the shut-down of the pile will add a considerable percentage to the C^{14} assay.

III. **The Concentration Effect and Its Relation to the Wigner Effect**

A. **Experimental Evidence**

When this investigation was begun in February the thought was in mind that a type of Szilard-Chalmers "hot atom" concentration of the C^{14} produced by the $C^{13}(n, \gamma)C^{14}$ reaction would occur. Discussion of this possibility with the group investigating the Wigner effect (particularly Drs. Simpson and Neubert, to both of whom we are heavily indebted) led to a reversal of this opinion, however, because of their demonstration that about 95% of the atoms displaced by the recoil from high energy neutrons (Wigner effect) had returned to lattice positions. They further explained that about 25% of all atoms in the graphite had been displaced at one time or another. In other words, the graphite after about 15 months exposure had about 75% of its atoms that had never been displaced at any time, about 24% that had been displaced and returned to the lattice, and about 1% in a displaced condition. This situation, at first sight, made the prospects of a successful concentration of the C^{14} by burning or other chemical reaction seem quite unlikely, and the attempt was

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set aside until a large effect of just this sort was disco-
vered accidentally late in May. Further, and more careful,
consideration of the information given us about the Wigner
effect then led to an understanding of how the C^{14} concen-
tration effect could exist even if 95% of the displaced atoms
had returned to a lattice position.

Before discussing this theory of the concentration
effect and its relation to the Wigner effect, we shall pro-
ceed to outline typical experimental evidence for the con-
centration effect. Langsdorf had studied C^{14} production in
graphite in evaluating the C^{13} slow neutron capture cross-
section. His data seemed to indicate that the concentration
of C^{14} in old pile graphite might well be large enough to
render obsolete graphite piles extremely valuable as a source
of radiocarbon. It was decided to conduct a careful assay of
typical graphite samples by burning them completely to CO_2 and
determining the absolute specific activity of the chemically
purified CO_2 by placing it in the gas of a Geiger counter so
no serious questions of counter efficiency, geometry, etc.,
would be involved. The sample was obtained from Hanford in
early May through the kind efforts of Dr. Daniels and the
hearty cooperation of Drs. Simpson and Neubert. It was a

cylindrical rod about 3" in diameter and 3' long, which had been in position in a remote part of the test hole of one of the piles since the beginning. Samples were sawed off by Dr. Neubert for his Wigner effect studies, and we took the sawdust as a convenient starting sample for the assay combustion. A gram or so was mixed with about equal weight of CuO, placed in a combustion tube and heated gradually to a temperature around 400°C, with O_2 gas running through and over the sample and then bubbling through saturated $Ba(OH)_2$ solutions in traps to precipitate $BaCO_3$. In weighing the $BaCO_3$ it was found that the combustion had been only 15% complete. After construction of an improved furnace, runs were conducted with fresh graphite samples to various higher burning percentages, up to substantially complete burning (Mr. Robert Hentz kindly performed these and most of the other combustion runs). At the end of this series of experiments the samples were counted for rough assay by spreading an "infinitely thick" layer of $BaCO_3$ (thicker than 20 mg/cm^2, the maximum range of the C^{14} radiation) on sample cards and counting them in the first shelf position (about 2 or 3 mm from the window) of a thin window counter with a 3 mg/cm^2 mica window of 3 cm diameter. The results were most startling in that the first (15% com-

bustion) had about 3.5 times the specific activity of the last, and all others fell on a smooth curve at intermediate values. These data are shown in Figure 1. The ordinates are the counts per min. observed, and the abscissae the percentage combustion. The lower curve is the differential burning curve calculated from the data given for the "integral" curve. It represents the calculated specific activities of successive $BaCO_3$ samples obtained by burning a given graphite sample.

Finally an extensive run was carried out, in which the CO_2 was collected in small successive fractions, so as to determine the variation of C^{14} content as the burning proceeded. The run was carried out in the following manner. Two grams of graphite contained in a Vycor tube were heated to 800°C in a small furnace. Oxygen was passed slowly over the sample, and then over copper oxide in a second furnace at 400°C, to oxidize any CO that might have been formed to CO_2. The gas was then passed through a series of bubblers containing varying amounts of $BaCl_2$ in NH_4OH solution. The bubblers were so arranged that as soon as one became saturated, as indicated by incipient cloudiness in the following bubbler, it could be by-passed and removed from the stream. This avoid-

Figure 1
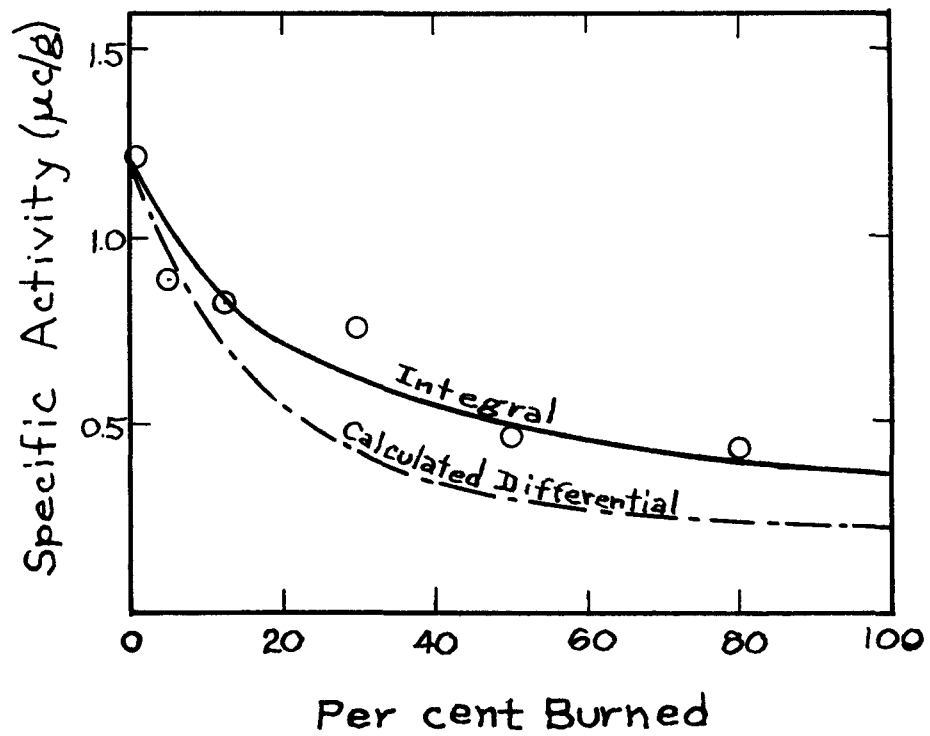
Integral Burning Curve
for
Hanford Graphite

ed the danger of an exchange reaction between the precipitated $BaCO_3$ and CO_2 gas. The precipitates were filtered, washed and dried. Thirteen fractions were collected and counted as described in the final section.

In addition, as a check on relative accuracy of the counting, measurements were made on a thin-windowed bell type counter, using an infinitely thick layer of $BaCO_3$. The results, which agreed with an average deviation of 5%, are shown in Figure 2 and assembled in Table II.

Because of a possible interchange of samples the apparent rise in activity between 30% and 60% burning may well be spurious. The general characteristics of the burning curve, that is, an initial sharp rise and fall, a plateau in the middle region, and a decrease at the end, seem to be well established. The differential curve calculated from Figure 1 agrees well with this curve, an interesting fact since the first curve was obtained with CuO as a combustion aid, and the second at higher temperature in the absence of CuO.

Figure 2
Differential Burning Curve
for
Hanford Graphite
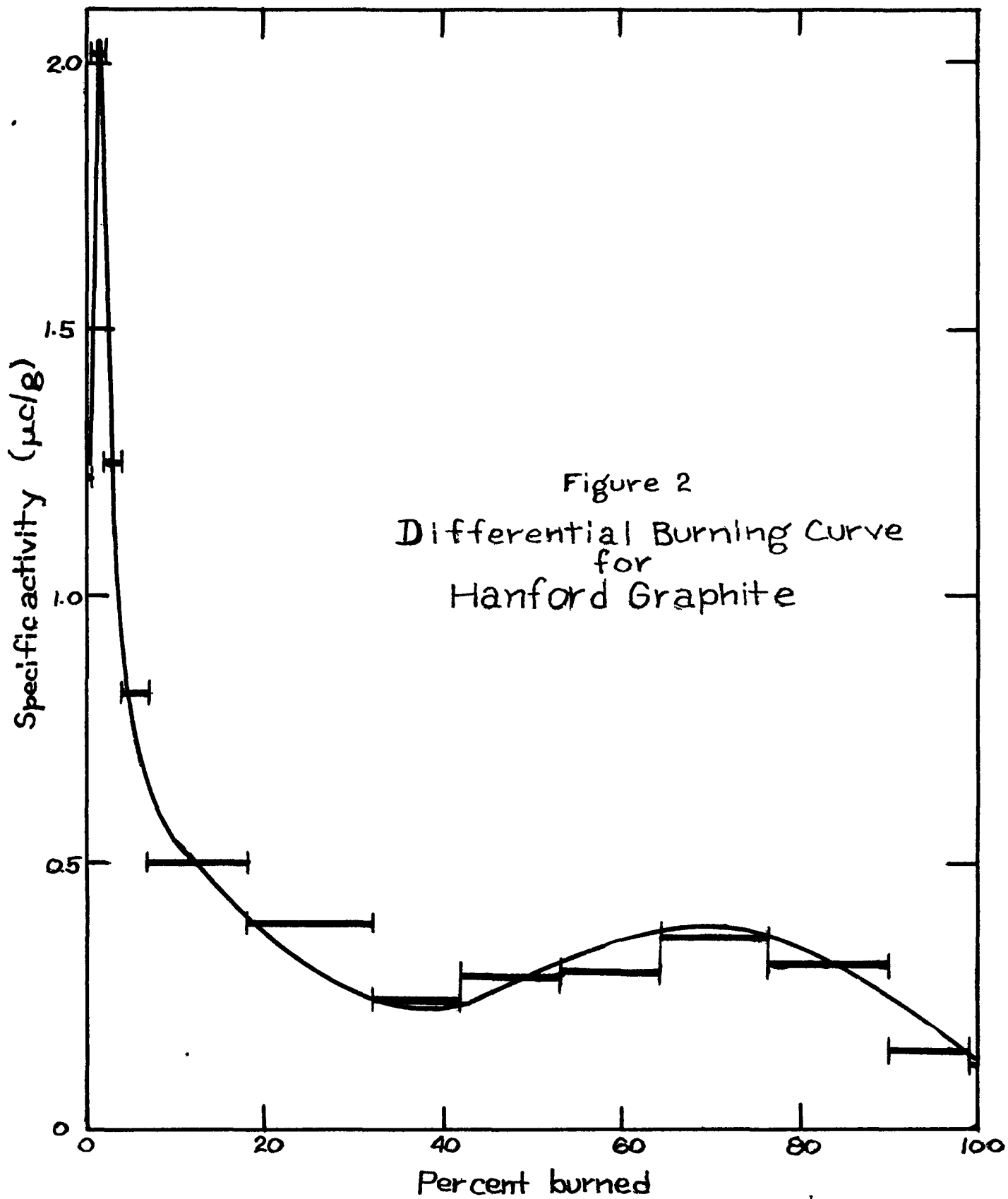
TABLE II

Stepwise Burning of Hanford Graphite

Sample	% Burned in Sample*	Cumulative % Burned	$\mu c/gm$ in Sample	Cumulative Average $\mu c/gm$
1	0.24%	0.24%	1.22	1.22
2	1.2	1.4	2.10	1.95
3	2.4	3.8	1.25	1.51
4	3.2	7.0	0.82	1.20
5	11.3	18.3	0.50	0.76
6	13.2	31.5	0.39	0.61
7	10.2	41.7	0.25	0.52
8	11.4	53.1	0.29	0.47
9	10.7	63.8	0.30	0.44
10	12.8	76.6	0.36	0.43
11	12.7	89.3	0.31	0.41
12	10.4	99.7	0.15	0.38
13	0.34	100.0	0.13	0.38

* The total amount of gas actually collected corresponded to only 88.1% because of the handling losses which are multiplied by the large number of samples. Since the combustion was carried to zero residue, the losses have been uniformly distributed among the samples.

By taking the area of the curve above the plateau value (0.3 μc/gm) we find that about 30% of the activity is removable in this region of activity, while the area above the final value of 0.12 μc/gm is 70% of the total activity. The tentative theoretical treatment of this behavior will be taken up after a discussion of the chromic acid oxidation experiments.

The choice of CrO_3 in concentrated sulfuric acid as a selective oxidant for C^{14}, suggested by Professor Franck, was dictated by two chief considerations. In the first place it was desired to avoid the healing and recovery processes occurring at high temperatures, which might operate to decrease the selectivity of oxidation. Secondly, statements in the literature[4] that chromic acid in 100% sulfuric penetrated between the crystal planes of natural graphite indicated the possibility that carbon atoms lying between the crystal planes might be selectively attacked at a reasonable rate. The reagent also possesses a very low vapor pressure, making it suitable for vacuum system work.

In the first series of experiments 76 mg of the graphite were placed in a bulb at liquid N_2 temperature together with

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[4]Riley, H., Fuel in Science and Practice, Vol. XXIV, p. 8,43.

1 g Na_2CrO_4 and 10 cc concentrated H_2SO_4. The bulb was attached to the line through stopcock F (see Figure 3) and evacuated. On warming, a slow evolution of gas was observed, increasing in rate over a period of hours. After five hours, an amount of gas corresponding to combustion of 1.4% of the original graphite had been evolved. This was condensed (a small amount of non-condensible gas appeared) and fractionated. On counting a six-fold enrichment was found.

After four hours, a further 2.1% had evolved, which showed on counting an enrichment of 1.7-fold. The next sample, comprising a further 1.3% of the stoichiometric quantity of CO_2, showed no enrichment, and several further samples, bringing the total amount burned up to 20.2%, showed approximately normal concentration. Uncertainties in the background, and errors due to the use of the small Eck and Krebs counter, make these results less accurate than those of the burning series, but their general trend is clear.

Two further experiments were made, using the large counter to determine the earlier, high-enrichment portion of the curve. In the first, one gram of carbon was used, and CO_2 corresponding to 0.2% oxidation collected. This was diluted with 2.9 parts of inert CO_2 and counted. The sample was found to be 16-fold enriched. A residue of condensible

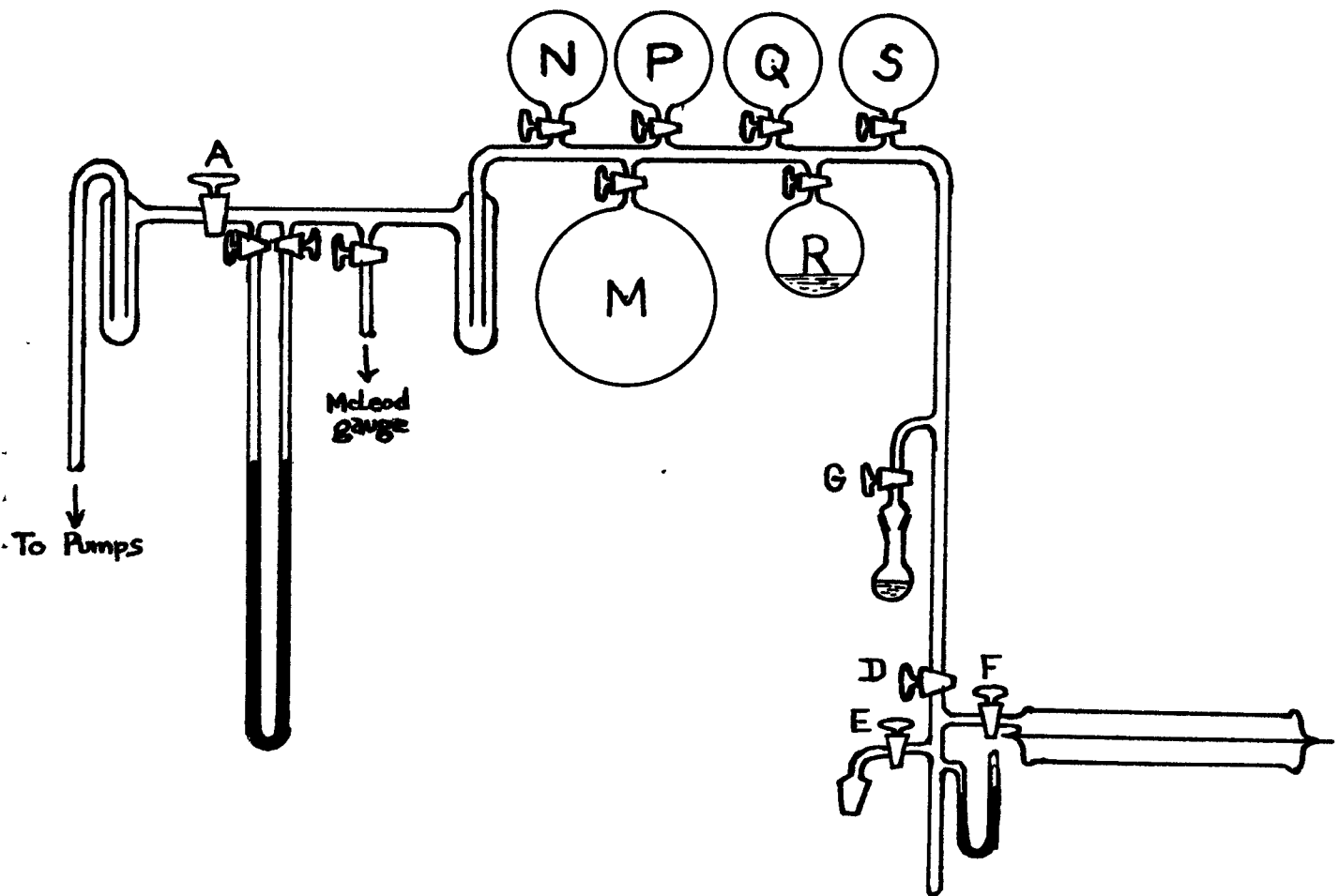Figure 3

radioactivity was found in this experiment, which caused a
large increase in counter background. In the second ex-
periment, using the same amount of carbon, CO_2 correspond-
ing to 0.02% oxidation was obtained. The enrichment obtained
in this experiment was more than 50-fold, corresponding to
a concentration of 20 $\mu c/gm$. Difficulty was again encount-
ered with a radioactive impurity, but successive fraction-
ation yielded results of satisfactory constancy.

B. <u>Theory of the Concentration Effect</u>

The following theory is intended only as a rough approx-
imation to the true behavior of graphite under irradiation,
the system being too complex to admit of exact treatment. It
is intended to provide a model for the enrichment process.

Let us suppose that in the course of irradiation in the
pile a fraction f of the carbon atoms in the graphite lattice
have been displaced by Wigner effect (f has been estimated
at 25% for bar R by Dr. Neubert), and have returned to lat-
tice positions, i.e., recovered. A small fraction g, estim-
ated by Dr. Neubert at about 1%, have been displaced but are
not yet recovered. Let us further define x as the fraction
of the recovered atoms which have migrated to the edge of the
crystallites, and 1-x as the fraction which have returned
into holes left vacant by Wignerized atoms, and which are

therefore not found at or near the surface.

Let us further assume that the radiocarbon follows the Wigner displaced atoms perfectly, i.e., that the average fate of the C^{14} atoms thrown out of the lattice by recoil on emission of the capture gamma is the same as the average fate of atoms displaced by fast neutron collision. This assumption is probably very good in the region of small f, but will deviate increasingly as the number of atoms which have suffered more than one Wigner displacement becomes large.

The mechanism of O_2 combustion at high temperatures, which we shall assume involves no penetration of planes under these conditions, is a relatively uniform attack on crystal faces, the O_2 entering through the intergranular channels (which the diffusion measurements of Burton and surface area measurements indicate to be of the order of 1μ in width). The enrichment of C^{14} in the early part of the curve is then due only to a higher concentration of C^{14} in the outer layers, made up chiefly of recovered atoms which have migrated to the edges. In other words, the fast neutron displacement of lattice atoms leads to the reconstitution of the crystal faces with atoms which originally were internal. In this new surface material we find a considerable fraction of the radio-

carbon and at a higher concentration than the internal material because it is diluted solely by the relatively small amount of graphite "distilled" to the surface by the Wigner effect.

The chromic acid treatment opens the graphite planes, allowing the oxidant to penetrate and oxidize the small residual fraction of interstitial atoms which have not yet recovered and then to attack the main lattice more or less uniformly. The displaced atoms are oxidized preferentially due to the lower free energy of activation, for atoms in the displaced position. It follows from this theory that not over some 5% of the radiocarbon can be concentrated in this way because only this fraction is interstitial.

Formulating the O_2 combustion effect, we have that the fraction $\dfrac{fx}{f + g}$ of the radiocarbon will burn out (under perfect conditions of uniform crystal size, uniform burning rate, etc.) with a percentage fx of the total carbon, while the fraction $\dfrac{f(1-x) + g}{f + g}$ will burn out at a constant concentration with the remaining fraction 1-fx of the graphite. Therefore we expect the concentration factor for the first part of the curve to be

$$\frac{\dfrac{fx}{f+g} \cdot \dfrac{1}{fx}}{\dfrac{f(1-x)+g}{f+g} \cdot \dfrac{1}{1-fx}} \approx \frac{\dfrac{1}{.25}}{\dfrac{.24(1-x)+.01}{.25} \cdot \dfrac{1}{1-.24x}}$$

In practice, of course, due to varying crystallite size and varying combustion rate, the curve will be smudged out. If we take a value of the concentration factor given by the ratio of the maximum enrichment value to the final value (about 6), we get for x the value 42%, indicating that 42% of the atoms have recovered by migrating to the surface. (More recent data indicate higher x values) It should not be necessary to stress the magnitude of the errors involved in this calculation, but it is probably accurate enough to assure us that migration to the surface plays an important role in recovery after Wigner displacement. This is in agreement with other evidence obtained by Dr. Simpson and Dr. Neubert from their studies of Wigner effect. The calculation given is over-simplified in that no account has been taken of the debilitating effect on the concentratability of the radiocarbon of secondary fast neutron collisions with atoms which have been displaced once and have migrated to the crystal faces.

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Similarly, the probability of migration, x, must necessarily vary with time of exposure, there being essentially no holes present at the beginning. These refinements obviously must be made in a more careful application of the radiocarbon phenomena to the problem of the exact mechanism of the Wigner effect, but they seem somewhat out of place in this report.

Two important predictions follow from the present theory: Since the surface atoms are part of the graphite lattice, we can predict that there will be <u>no reduction in the oxygen combustion concentration effect</u> caused by the annealing necessary to remove the lattice defect, effects which are manifest in so many ways, e.g., resistivity, in heavily irradiated graphite. Similarly, we expect that such annealing will indeed reduce the "cleaning solution" concentration effect because it is largely interstitial in nature and the interstitial atoms will resume lattice positions during the annealing.

Method of Gas Counting

Two types of counter were used in this work. The first was a thin-walled Eck and Krebs counter of standard design, with tungsten wire anode and silver cathode. This counter

had an estimated effective counting volume of 18.5 cc (the volume enclosed in the cathode cylinder) It suffered from three disadvantages: (1) its small volume made the introduction of large quantities of gas into the counter difficult; (2) the effective counting volume was badly defined; and (3) when radioactive impurities were adsorbed on the walls, raising the background to an undesirably high level, the tube had to be abandoned. To obviate these difficulties a counter was constructed consisting of a brass cylinder, 45 mm inside diameter and 30 cm in length, fitted with a pair of glass caps through the center of which was threaded the anode wire, the whole being vacuum sealed by means of a special De Khotinsky-type wax. A spring under tension outside the counter at one end served to hold the wire taut, and a stopcock and ground joint connected the counter to the vacuum line. A number of interchangeable cylinders and caps were used, so that the counter could be dismantled and reassembled readily. This design proved rugged and reliable in practice. The effective counting volume of the large counter was taken as 477 cc, the small volume of the end-pieces minimizing the uncertainty in this value.

The vacuum line used in this work is shown in Figure 3. The five-liter bulb M contained argon, the bulb R ethanol,

and the other bulbs such other inert and radioactive gases
as it was necessary to store.

The technique of counting CO_2, obtained from burning
the Hanford graphite in oxygen, was as follows. About 50
mg of dried $BaCO_3$ were weighed into a small bulb with ground
joint. The bulb was chilled in liquid N_2, and 2 cc concentra-
ted H_2SO_4 added. The bulb, surrounded by a liquid N_2 bath,
was then placed on the line, and evacuated through stopcock 6.
When a satisfactory vacuum, as measured on the McLeod gauge,
had been reached, the manifold was closed off by means of stop-
cocks A and D, and the bulb allowed to warm. The CO_2 was
liberated smoothly over a period of about five minutes. The
stopcock G was then closed, the gas condensed by means of li-
quid N_2 in the manifold trap, and stopcock A opened momen-
tarily, to remove any non-condensible impurities which might
be present. Stopcock A was then closed, and the system allow-
ed to warm to room temperature. The pressure was then read
on the large manometer. Stopcock D was now opened, permit-
ting the gas to flow into the small manometer system and
counter. In experiments where small quantities of gas were
employed, the gas was condensed and measured in the small
manometer system, which had a volume of only about 15 cc. The

pressure of CO_2 in the counter was calculated from the known volumes of counter, small manometer system, and manifold.

After closing stopcock E, the remaining sample in the manifold was condensed back into the acid bulb, for further use if necessary. Sufficient ethanol was then put in the manifold to introduce 2 cm pressure of ethanol into the counter. Stopcock E was opened to permit the ethanol to flow into the counter, and then rapidly closed. The ethanol in the manifold was pumped out, and sufficient argon added, in the same fashion, to bring the pressure up to 20 cm. After filling about five minutes were necessary to allow the contents of the counter to mix thoroughly.

The low pressures (less than 1 cm) of CO_2 used in these experiments did not hinder successful gas counting. The plateau was located at about 1500 volts, and averaged 100-150 volts in length. In normal practice, the optimum counting voltage was found by means of an oscilloscope. To insure that the counter was operating at satisfactory efficiency, a small external $Th(NO_3)_4$ standard was used, the number of counts produced by this standard being referred to a 2.0 cm ethanol plus 18.0 cm argon filling as 100% efficiency. The counting efficiency of the CO_2-filled counter was almost al-

ways between 95% and 105%. The counting was continued for a sufficient time to reduce the root-mean-square of all random counting errors to about 5% or less. The natural background of the counter was measured before and after counting a group of active CO_2 samples by filling with the standard argon-ethanol mixture.